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# Ag<sub>3</sub>PO<sub>4</sub> nanocrystals and g-C<sub>3</sub>N<sub>4</sub> quantum dots decorated Ag<sub>2</sub>WO<sub>4</sub> nanorods: ternary nanoheterostructures for photocatalytic degradation of organic contaminants in water†

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Visible-light-driven Ag<sub>3</sub>PO<sub>4</sub>/graphite-like carbon nitride/Ag<sub>2</sub>WO<sub>4</sub> photocatalysts with different weight fractions of Ag<sub>3</sub>PO<sub>4</sub> were synthesized. Ag<sub>2</sub>WO<sub>4</sub> nanorods with a scale of 500 nm to 3 μm were prepared by using a hydrothermal reaction. Via a facile deposition–precipitation technique, graphite-like carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) quantum dots and Ag<sub>3</sub>PO<sub>4</sub> nanocrystals were then deposited onto the surface of Ag<sub>2</sub>WO<sub>4</sub> nanorods sequentially. Under visible-light irradiation (λ > 420 nm), the Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>WO<sub>4</sub> nanorods degraded Rh B efficiently and displayed much higher photocatalytic activity than that of pure Ag<sub>2</sub>WO<sub>4</sub> and the g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>WO<sub>4</sub> composite, and the Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>WO<sub>4</sub> hybrid photocatalyst with 30 wt% of Ag<sub>3</sub>PO<sub>4</sub> exhibited the highest photocatalytic activity. The quenching effects of different scavengers demonstrated that reactive h<sup>+</sup> and ·O<sup>2-</sup> played the major roles in Rh B degradation. It was elucidated that the excellent photocatalytic activity of Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>WO<sub>4</sub> for the degradation of Rh B under visible light (λ > 420 nm) can be ascribed to the efficient separation of photogenerated electrons and holes through the Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>WO<sub>4</sub> heterostructure.

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## 1. Introduction

The development of visible-light-driven photocatalysts with excellent performance and good stability is a precondition for harvesting more sunlight and realizing efficient photocatalysis. In recent years, Ag-based photocatalysts, such as AgX (where X = Cl, Br, and I), Ag<sub>2</sub>O, Ag<sub>2</sub>CO<sub>3</sub>, Ag<sub>6</sub>Si<sub>2</sub>O<sub>7</sub>, Ag<sub>2</sub>WO<sub>4</sub>, Ag<sub>3</sub>PO<sub>4</sub>, and Ag<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, have been developed for photocatalysis applications.<sup>1–8</sup> Among those Ag-based photocatalysts, Ag<sub>2</sub>WO<sub>4</sub> has been the most studied because of its weak crystal field and was verified to exhibit H<sub>2</sub> evolution and organic pollution degradation ability under UV light irradiation.<sup>9</sup> However, the band gap of Ag<sub>2</sub>WO<sub>4</sub> is theoretically calculated to be 3.55 eV, resulting in its sluggish reaction to visible light, like TiO<sub>2</sub>.<sup>10</sup> Thereupon, many efforts have been devoted to make Ag<sub>2</sub>WO<sub>4</sub> sensitive to visible light, including its combination with sensitizers, *i.e.*, AgI, Ag/AgCl, and Ag. Unfortunately, Ag<sub>2</sub>WO<sub>4</sub> itself has not yet been modified to be sensitive to visible light.<sup>11–13</sup> However, some researchers found that Ag<sub>3</sub>PO<sub>4</sub> shows strong oxidation power, which can achieve quantum efficiency of up to 90% under visible light for O<sub>2</sub> generation from water splitting.<sup>14,15</sup> However,

as Ag<sub>3</sub>PO<sub>4</sub> is light-sensitive and slightly soluble in aqueous solution, it will be photocorroded and decompose to weakly active Ag during the photodegradation, and, accordingly, the photocatalytic activity gradually deteriorates, which is the main hindrance for the practical application of Ag<sub>3</sub>PO<sub>4</sub> as a recyclable and highly efficient photocatalyst. Recent reports have shown that forming complexes with special structures such as core-shell nanostructures, plasmonic structures, and heterostructures could not only effectively protect the Ag<sub>3</sub>PO<sub>4</sub> crystals from dissolution in aqueous solutions but also enhance their stabilities and photocatalytic performance.<sup>15,16</sup> Therefore, modifying Ag<sub>2</sub>WO<sub>4</sub> with Ag<sub>3</sub>PO<sub>4</sub> could significantly accelerate the transfer of photogenerated charge carriers.

Nowadays, graphite-like carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has been studied as a promising candidate for hydrogen evolution and environment purification under visible-light irradiation.<sup>17–19</sup> Although g-C<sub>3</sub>N<sub>4</sub> possesses good chemical and thermal stability, its use in photocatalysis is limited because of its high recombination of photogenerated electron–hole pairs.<sup>20</sup> To solve this problem, abundant strategies, including doping, deposition, and sensitization, were developed.<sup>20–23</sup> Constructing the heterostructure is also an effective approach for decreasing the recombination rate of photogenerated charges. However, most of the reported g-C<sub>3</sub>N<sub>4</sub> nanostructures are composed of stacked two-dimensional nanosheets, and very few available examples concentrating on zero-dimensional quantum dots (QDs) exist, especially on QD-based heterostructures.<sup>19,24</sup> Given the

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enhanced light absorption and, more importantly, excellent electron conductivity of carbon materials, it is rationally speculated that decoration of  $\text{Ag}_2\text{WO}_4$  with  $g\text{-C}_3\text{N}_4$  QDs in an intimate integration fashion would significantly improve the photocatalytic performances of  $\text{Ag}_2\text{WO}_4$ .

Herein, we report a successful attempt at the preparation of  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  nanoheterostructures via a facile *in situ* precipitation synthetic strategy. The photocatalytic performance of the ternary composite was investigated by measuring the photodegradation of rhodamine B (Rh B) under visible-light irradiation ( $\lambda > 420$  nm). Up to date, construction of  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  ternary heterostructures in combination with a systematic study on the photocatalysis mechanism has not yet been reported.

## 2. Experimental

### 2.1 Preparation of photocatalysts

**2.1.1 Preparation of  $\text{Ag}_2\text{WO}_4$  nanorods.** All reagents for synthesis and analysis were commercially available and used without further treatments. The  $\text{Ag}_2\text{WO}_4$  nanorods were synthesized through a facile hydrothermal method. In a typical procedure, a solution of  $\text{Na}_2\text{WO}_4$  ( $0.10 \text{ mol L}^{-1}$ ,  $10 \text{ mL H}_2\text{O}$ ) was stirred for 30 min, then  $20 \text{ mL}$  aqueous solution of  $\text{AgNO}_3$  ( $0.40 \text{ mol L}^{-1}$ ,  $5 \text{ mL H}_2\text{O}$ ) was dropped slowly into the above solution, which was stirred magnetically for another 30 min. The mixed solution was transferred into a  $20 \text{ mL}$  Teflon-lined steel autoclave, which was heated in an oven at  $160 \text{ }^\circ\text{C}$  for 24 h. Then the system was allowed to cool to room temperature naturally. Lastly, the obtained samples were collected and washed with ethanol and distilled water several times then and dried at  $70 \text{ }^\circ\text{C}$  for 2 h.

**2.1.2 Preparation of  $g\text{-C}_3\text{N}_4$  QDs.** Bulk  $g\text{-C}_3\text{N}_4$  was prepared by heating melamine for 4 h to  $550 \text{ }^\circ\text{C}$  and keeping it at this temperature for another 4 h in air.<sup>24</sup>  $g\text{-C}_3\text{N}_4$  QDs was prepared by using Yu's method:<sup>24</sup> First,  $1 \text{ g}$  of bulk  $g\text{-C}_3\text{N}_4$  was treated in the mixture of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) ( $20 \text{ mL}$ ) and nitric acid ( $\text{HNO}_3$ ) ( $20 \text{ mL}$ ) for  $\sim 2$  h at room temperature. The mixture was then diluted with deionized water ( $1 \text{ L}$ ) and washed several times. Second,  $50 \text{ mg}$  of the obtained solid was dispersed in  $30 \text{ mL}$  concentrated  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , and then the mixed suspension was transferred into a  $20 \text{ mL}$  Teflon-lined stainless-steel autoclave and heated at  $200 \text{ }^\circ\text{C}$  for 24 h. Upon cooling to room temperature, the precipitate was washed with water several times to remove the adsorbed  $\text{NH}_3$  molecules. Third,  $10 \text{ mg}$  of the synthesized solid was dispersed in  $100 \text{ mL}$  of water, and then treated ultrasonically for  $\sim 6$  h. The as-obtained aqueous suspension was then centrifuged at  $\sim 7000$  rpm and dialyzed in a dialysis bag to remove large-sized nanoparticles.

**2.1.3 Preparation of  $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  photocatalyst.** The as-prepared  $\text{Ag}_2\text{WO}_4$  nanorods ( $300 \text{ mg}$ ) were mixed with  $200 \text{ mL}$  of deionized water by ultrasonication for 30 min. Then,  $1.0 \text{ mL}$  of a 5% polyethylene glycol (PEG) 2000 solution was added and the dispersion was stirred for another 10 min. For wrapping  $g\text{-C}_3\text{N}_4$  QDs on  $\text{Ag}_2\text{WO}_4$  nanorods,  $30 \text{ mL}$  of the  $g\text{-C}_3\text{N}_4$  QDs solution ( $1 \text{ mg mL}^{-1}$ ) was added and the reaction temperature was kept at  $70 \text{ }^\circ\text{C}$  for 60 min. The resulting suspension was

filtered, washed with deionized water three times, and dried at  $60 \text{ }^\circ\text{C}$  for 24 h in a vacuum oven. The theoretical wrapping amount of  $g\text{-C}_3\text{N}_4$  QDs was 10 wt%.

**2.1.4 Preparation of  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  photocatalyst.** The  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  hybrid photocatalyst was synthesized through an *in situ* precipitation method at room temperature. In a typical process,  $g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  nanorods ( $300 \text{ mg}$ ) were dispersed in  $100 \text{ mL}$  of deionized water by ultrasound for 30 min, and then an emulsion of  $\text{AgNO}_3 + \text{Na}_2\text{HPO}_4$  (with a molar ratio of  $\text{Ag} : \text{P} = 3 : 1$ ) was dropwise added to the suspension under magnetic stirring. The pH value was adjusted to 3 by adding  $1.0 \text{ M}$  NaOH. The resulting suspension was stirred in the dark for another 30 min. Finally, the precipitate was washed with deionized water three times, collected by centrifugation, and then dried at  $60 \text{ }^\circ\text{C}$  in the vacuum drying oven to obtain  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  (denoted as 10%  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ , 20%  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ , 30%  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ , 40%  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ , and 50%  $\text{Ag}_3\text{PO}_4/g\text{-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ , respectively).

### 2.2 Characterization of photocatalysts

X-ray diffraction (XRD) was performed on a D/MAX 2500 V diffractometer (Rigaku, Japan) with monochromatized  $\text{Cu K}_\alpha$  radiation,  $\lambda = 0.15418 \text{ nm}$ , and the scanning range was from  $10^\circ$  to  $70^\circ$ . The morphologies and microstructures of the products were characterized by transmission electron microscopy (TEM, JEM-2100F). X-ray photoelectron spectroscopy (XPS, VG Scientific) using  $300 \text{ W Al K}_\alpha$  radiation as the excitation source was applied to study the composition and chemical state of the elements. Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained with an FT-IR spectrometer (America Perkin Elmer, Spectrum One) using the standard KBr disk method. UV-vis diffuse reflection spectra (DRS) of the samples were tested on a scan UV-vis spectrophotometer (UV-2550) equipped with an integrating sphere using  $\text{BaSO}_4$  as the reference sample. The surface areas were measured by using the nitrogen adsorption Brunauer–Emmett–Teller (BET) method (BET/BJH Surface Area, 3H-2000PS1).

### 2.3 Photocatalytic activities study

The photocatalytic properties of the as-prepared samples were evaluated using Rh B as a model compound. In experiments, the Rh B solution ( $0.01 \text{ mmol L}^{-1}$ ,  $100 \text{ mL}$ ) containing  $0.02 \text{ g}$  of photocatalyst were mixed in a Pyrex reaction glass. The reactivity experiments were conducted in air at room temperature. A  $300 \text{ W Xe}$  lamp ( $\lambda > 420 \text{ nm}$ ) with  $100 \text{ mW cm}^{-2}$  illumination intensity was employed to provide visible-light irradiation. A  $420 \text{ nm}$  cutoff filter was inserted between the lamp and the sample to filter out UV light ( $\lambda < 420 \text{ nm}$ ). Prior to visible-light illumination, the suspension was strongly stirred in the dark for 40 min. Then the solution was exposed to visible-light irradiation under magnetic stirring. At given time intervals,  $4 \text{ mL}$  of the suspension was periodically collected and analyzed after centrifugation. The Rh B concentration was analyzed by using a UV-2550 spectrometer to record the intensity of the maximum band at  $552 \text{ nm}$  in the UV-vis absorption spectra.



## 2.4 Active species trapping experiments

For detecting the active species during photocatalytic reactivity, some sacrificial agents, such as 2-propanol (IPA), disodium ethylenediamine tetraacetic acid (EDTA-2Na), and 1,4-benzoquinone (BQ) were used as the hydroxyl radical ( $\cdot\text{OH}$ ) scavenger, hole ( $\text{h}^+$ ) scavenger, and superoxide radical ( $\text{O}_2^{\cdot-}$ ) scavenger, respectively. The method was similar to the former photocatalytic activity test with the addition of 1 mmol of quencher in the presence of Rh B.

## 3. Results and discussion

To determine the crystal form of as-prepared samples, the XRD patterns were recorded, as shown in Fig. 1. Pure  $\text{Ag}_2\text{WO}_4$  shows obvious diffraction peaks at  $2\theta = 30.2^\circ$ ,  $31.4^\circ$ ,  $33.0^\circ$ , and  $45.4^\circ$ , which are attributed to the (002), (231), (400), and (402) diffraction planes of  $\alpha\text{-Ag}_2\text{WO}_4$  (JCPDS no. 34-0061), respectively.<sup>25</sup> For the pure  $\text{g-C}_3\text{N}_4$  sample, the diffraction peak at  $27.4^\circ$  can be clearly observed, which is indexed to (002) plane of  $\text{g-C}_3\text{N}_4$ .<sup>26</sup> From the XRD pattern of the  $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite, all the crystal planes of  $\alpha\text{-Ag}_2\text{WO}_4$  can be detected. However, there are no any diffraction peaks of  $\text{g-C}_3\text{N}_4$  that can be observed for the  $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  sample, owing to small crystal size of  $\text{g-C}_3\text{N}_4$  QDs.<sup>26</sup> For the pure  $\text{Ag}_3\text{PO}_4$ , the diffraction peaks can be indexed to the cubic structure of  $\text{Ag}_3\text{PO}_4$  (JCPDS 06-0505). The diffraction peaks of  $\text{Ag}_3\text{PO}_4$  are clearly observed in  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composites, and the intensities of the diffraction peaks of  $\text{Ag}_3\text{PO}_4$  increase with increasing weight ratio of  $\text{Ag}_3\text{PO}_4$  in the composites.

Herein, the successful loading of  $\text{g-C}_3\text{N}_4$  QDs was illustrated by FT-IR spectra, as displayed in Fig. 2. The main characteristic peaks of  $\text{g-C}_3\text{N}_4$  QDs are observed in both  $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  and  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  spectra, showing the successful loading of  $\text{g-C}_3\text{N}_4$  QDs. The absorption bands at  $1700\text{--}800\text{ cm}^{-1}$  are attributed to either  $\text{C}=\text{N}$  or  $\text{C}-\text{N}$  stretching vibrations.<sup>19</sup> The broad range centered at  $3200\text{ cm}^{-1}$  can be ascribed to the  $\text{N}-\text{H}$  stretching vibration.<sup>19</sup>

XPS measurement was also employed to investigate the surface chemical states of the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite. Fig. 3a shows the XPS spectrum of Ag 3d; two

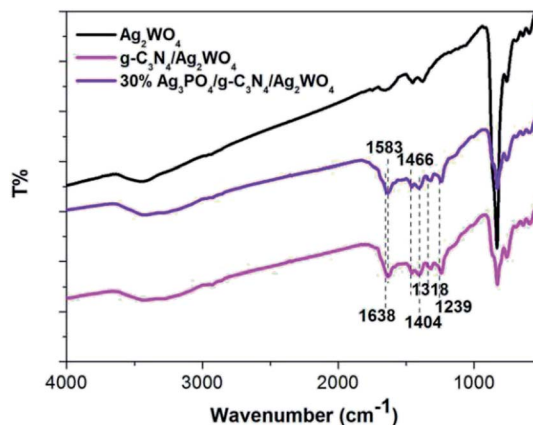


Fig. 2 FT-IR spectra of the as-prepared samples.

different peaks centered at binding energies of 366.5 and 372.6 eV can be detected, and these are assigned to  $\text{Ag } 3d_{5/2}$  and  $\text{Ag } 3d_{3/2}$ ,<sup>27</sup> respectively. The XPS spectrum of W 4f shows two different peaks centered at 38.3 and 36.1 eV, which are ascribed to  $\text{W } 4f_{5/2}$  and  $\text{W } 4f_{7/2}$ , respectively (Fig. 3b).<sup>26</sup> The P 2p peak is observed at  $\sim 134.1$  eV (Fig. 3c), corresponding to  $\text{P}^{5+}$ .<sup>27</sup> As can be seen in the XPS spectrum of C 1s (Fig. 3d), the peak at 283.3 eV can be assigned to the  $\text{sp}^2$ -bonded carbon in  $\text{C}-\text{C}$ , whereas the peak located at 287.0 eV reveals the formation of  $\text{N}-\text{C}=\text{N}$ .<sup>19</sup> The XPS spectrum of N 1s can be deconvoluted into two peaks with binding energies at 397.5 and 400.0 eV, which are attributed to  $\text{C}-\text{N}=\text{C}$  and  $(\text{N}-\text{C})_3$ ,<sup>19</sup> respectively.

Fig. 4 shows scanning electron microscopy (SEM) images of pure  $\text{Ag}_2\text{WO}_4$  and the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite. Fig. 4a shows a rod-like structure, and the average diameter of the nanorods was  $\sim 100$  nm. The  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite displays a similar morphology to that of pure  $\text{Ag}_2\text{WO}_4$  (Fig. 4b), showing that loading  $\text{Ag}_3\text{PO}_4$  nanocrystals and  $\text{g-C}_3\text{N}_4$  QDs did not have any significant influence on the morphology of the  $\text{Ag}_2\text{WO}_4$  nanorods. The as-prepared  $\text{Ag}_3\text{PO}_4$  sample was composed of nanocrystals with average sizes of  $\sim 20$  nm (Fig. S1†). A TEM image of  $\text{g-C}_3\text{N}_4$  QDs is shown in Fig. S2,† revealing that the prepared  $\text{g-C}_3\text{N}_4$  QDs are mono-dispersed in the water solution and that each QD is uniform in size. Fig. 4c shows a TEM image of an individual  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  nanorod. It can be seen that  $\text{Ag}_3\text{PO}_4$  nanocrystals and  $\text{g-C}_3\text{N}_4$  QDs were loaded on the surface of the  $\text{Ag}_2\text{WO}_4$  nanorod. A high-resolution TEM image of the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite reveals that the crystal lattice fringe patterns are  $\sim 0.336$  and  $\sim 0.213$  nm (Fig. 4d), which correspond to the (002) crystal plane of  $\text{g-C}_3\text{N}_4$  and the (210) crystal plane of  $\text{Ag}_3\text{PO}_4$ , respectively. The lattice distance of 0.229 nm in the nanorod is correlated to the (421) crystal plane of  $\text{Ag}_2\text{WO}_4$  (Fig. 4e).

The BET surface areas of pure  $\text{Ag}_2\text{WO}_4$  and  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  were analyzed using an automated surface area analyzer (Fig. 5). The calculated BET surface area of  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  is  $110.602\text{ m}^2\text{ g}^{-1}$ , which is larger than that of pure  $\text{Ag}_2\text{WO}_4$  ( $20.817\text{ m}^2\text{ g}^{-1}$ ). It can be concluded that the loading of  $\text{Ag}_3\text{PO}_4$  and  $\text{g-C}_3\text{N}_4$  QDs can facilitate more efficient

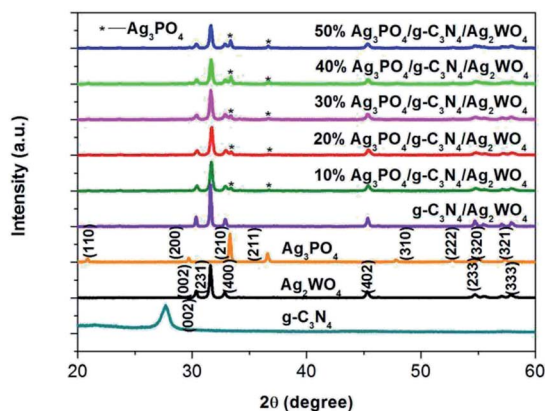


Fig. 1 XRD patterns of the as-prepared samples.



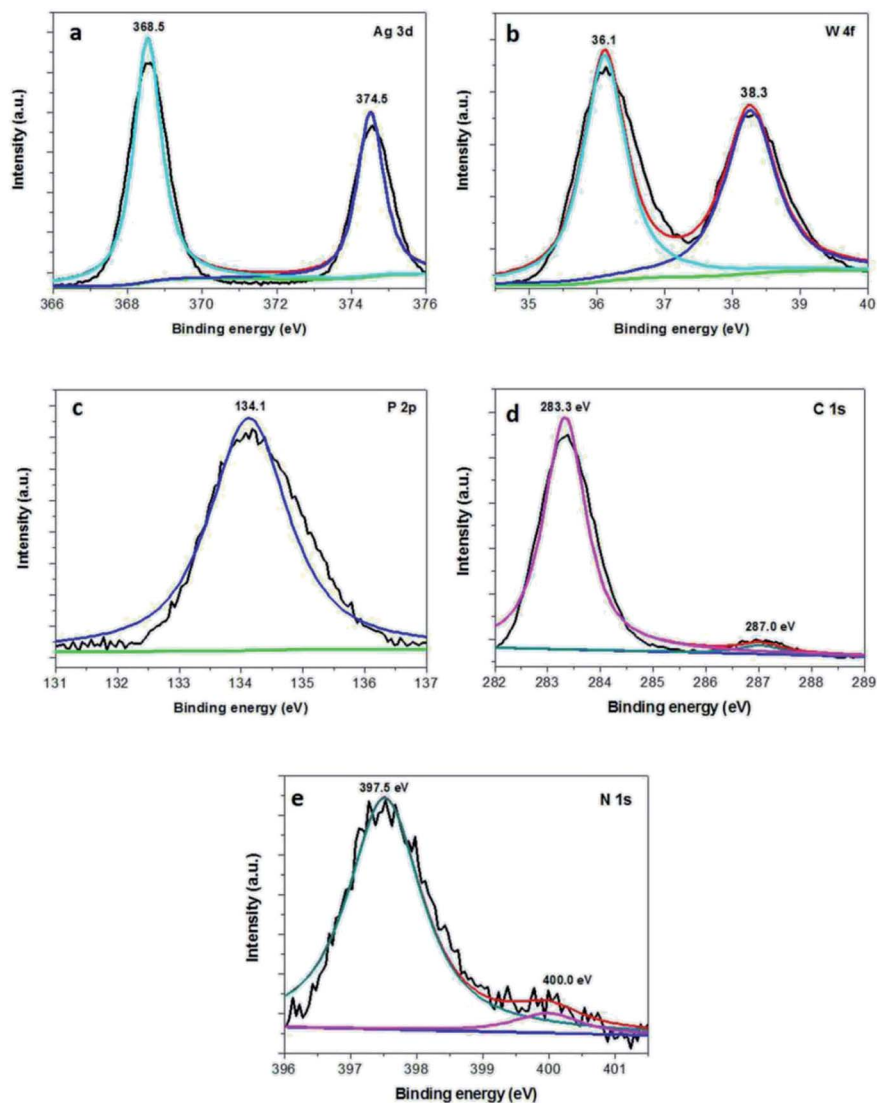


Fig. 3 XPS spectra of the as-obtained 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ : (a) Ag 3d, (b) W 4f, (c) P 3p, (d) C 1s, and (e) N 1s.

contact of the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite with organic contaminants, which is beneficial to the improvement of photocatalytic performance.<sup>19</sup>

UV-vis DRS are shown in Fig. 6 to study the optical absorption properties of the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite. The band gap of anatase  $\text{Ag}_2\text{WO}_4$  is  $\sim 3.20$  eV, so its absorption onset is located at 410 nm. The band gap for  $\text{g-C}_3\text{N}_4$  QDs is 2.75 eV, corresponding to the absorption onset of 450 nm. In addition, the band gap of  $\text{Ag}_3\text{PO}_4$  is calculated to be 2.13 eV, indicating an absorption onset at  $\sim 580$  nm. In comparison with pure  $\text{Ag}_2\text{WO}_4$ , the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite shows an absorption in the visible range that accompanies a red shift in the absorption edge resulting from the synergistic effect among  $\text{Ag}_2\text{WO}_4$ ,  $\text{Ag}_3\text{PO}_4$ , and  $\text{g-C}_3\text{N}_4$ . The results reveal that the obtained  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite could be employed as a visible-light photocatalyst. The chronoamperometric  $I-t$  curves are shown in Fig. S3.† Compared with pure  $\text{Ag}_2\text{WO}_4$ , the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite exhibited enhanced

photocurrent responses. The ternary nanoheterojunctions can facilitate photoelectron-hole separation and thus retard photoelectron-hole recombination in the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite.<sup>28–30</sup>

In this study,  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  along with sole  $\text{Ag}_2\text{WO}_4$  and  $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite was tested for photocatalytic Rh B degradation under visible-light irradiation (Fig. 7a). The blank experiment demonstrated that Rh B was stable under visible-light irradiation for 80 min. The pure  $\text{Ag}_2\text{WO}_4$  composite exhibited generally low photocatalytic performances, with only 40.0% Rh B degradation, after 80 min visible-light irradiation. The low performance is probably due to the fast recombination of photoinduced charges in the single  $\text{Ag}_2\text{WO}_4$ . Compared with the pure  $\text{Ag}_2\text{WO}_4$  sample, the  $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite exhibited enhanced photocatalytic efficiency (50% Rh B degradation). The photocatalytic activity of  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  further improved the degradation of Rh B under visible light ( $\lambda > 420$  nm), which can be ascribed to the



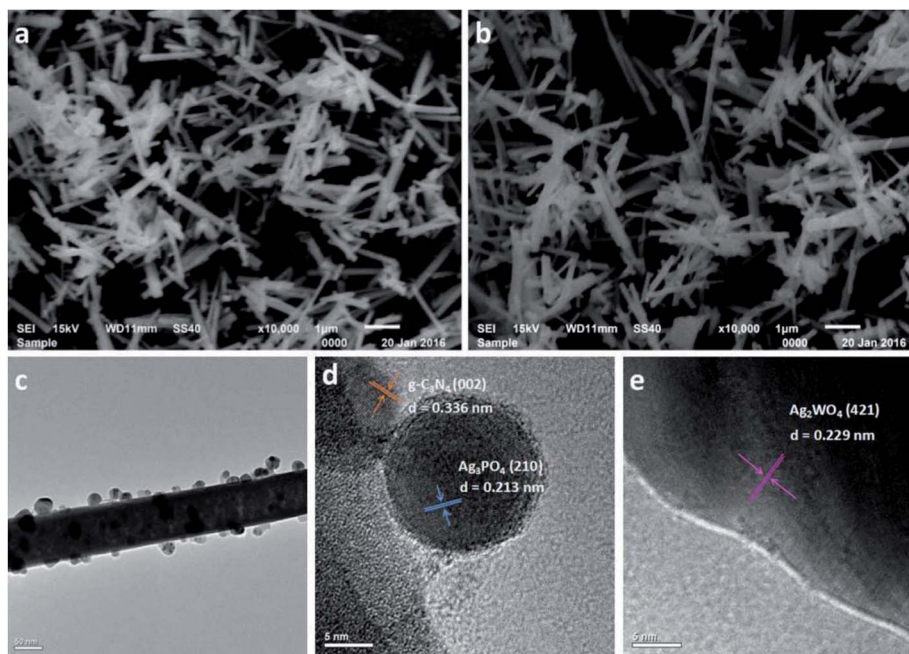


Fig. 4 SEM images of the as-prepared samples: (a)  $\text{Ag}_2\text{WO}_4$  and (b) 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ . (c) TEM image of 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ . (d and e) High-resolution TEM images of 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ .

efficient separation of photogenerated electrons and holes through the ternary heterostructure. Among the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  nanocomposites, the highest activity was obtained with the 30%  $\text{Ag}_3\text{PO}_4$  loading sample, with which almost 100% of Rh B was photodegraded after 80 min of visible-light irradiation. This is because hybridization of  $\text{Ag}_2\text{WO}_4$  with  $\text{Ag}_3\text{PO}_4$  can result in efficient separation of photogenerated charges, thus improving the photocatalytic performance. However, too many  $\text{Ag}_3\text{PO}_4$  can even cover the surface of  $\text{Ag}_2\text{WO}_4$ , which can reduce the density of active sites, thus reducing the photocatalytic efficiency. Therefore, the suitable loading content of  $\text{Ag}_3\text{PO}_4$  is a primary prerequisite for optimizing the photocatalytic reaction.

It is important to study the active species in the photocatalysis process. As shown in Fig. 7b, the photocatalytic efficiency of the 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite was greatly suppressed after the addition of BQ and EDTA-2Na, indicating that  $\text{O}_2^{\cdot-}$  and  $\text{h}^+$  were the main reactive species. In addition, a slight decrease in the photocatalytic activity was observed by the addition of IPA, suggesting that  $\cdot\text{OH}$  was not the main reactive species.

The stability of the 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  photocatalyst was studied through performing recycle experiments, as shown in Fig. 8. After four photocatalytic runs, the photocatalytic efficiency did not display any significant decay. The stability of the photocatalyst was also studied by using XRD (Fig. 9a) and SEM analysis (Fig. 9b) of fresh and used 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ . It can be seen that the phase structure, as well as the morphology of the 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ , remains intact after four recycles, revealing the high stability of the 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  photocatalyst.

Based on the results and discussion above, heterostructure formed in the  $\text{g-C}_3\text{N}_4/\text{Ag}/\text{BiVO}_4$  photocatalyst played an important role in the efficient separation of photoinduced charges. The potentials of VB and CB of a semiconductor can be calculated according to the following empirical equations:

$$E_{\text{VB}} = X - E^{\text{e}} + 0.5E_{\text{g}} \quad (1)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (2)$$

where  $E_{\text{VB}}$  is the valence band edge potential,  $E_{\text{CB}}$  is the conduction band edge potential,  $X$  is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms,  $E^{\text{e}}$  is the energy of free

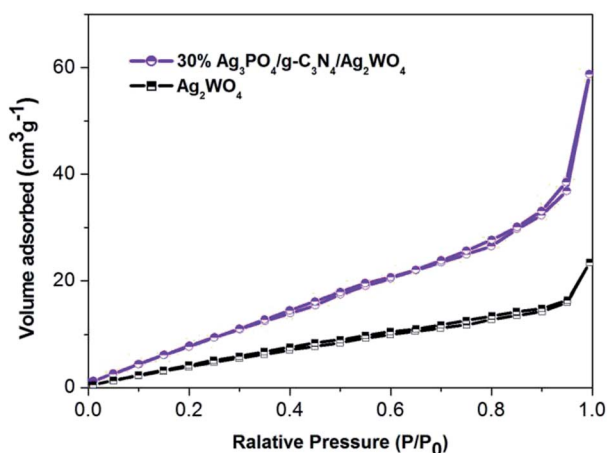


Fig. 5  $\text{N}_2$  adsorption-desorption isotherm curves of the as-prepared samples.



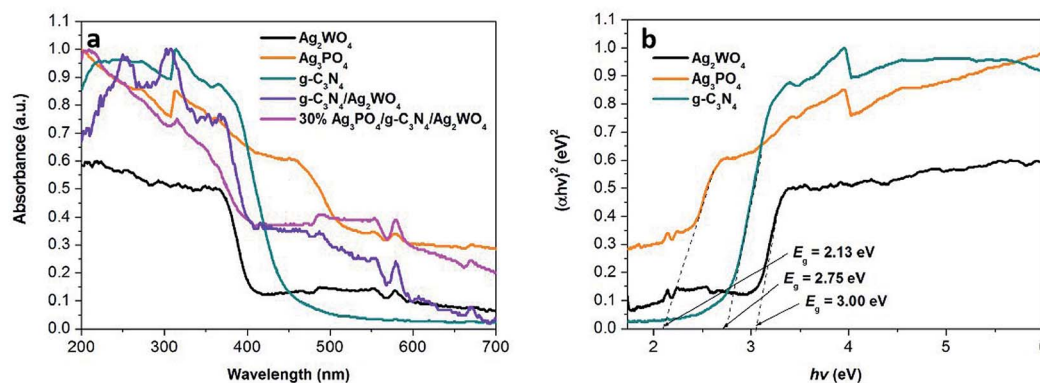


Fig. 6 UV-vis diffuse reflection spectra of the as-obtained samples. (b) Plots of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) for the band gap energies of  $\text{Ag}_3\text{PO}_4$ ,  $\text{g-C}_3\text{N}_4$ , and  $\text{Ag}_2\text{WO}_4$ .

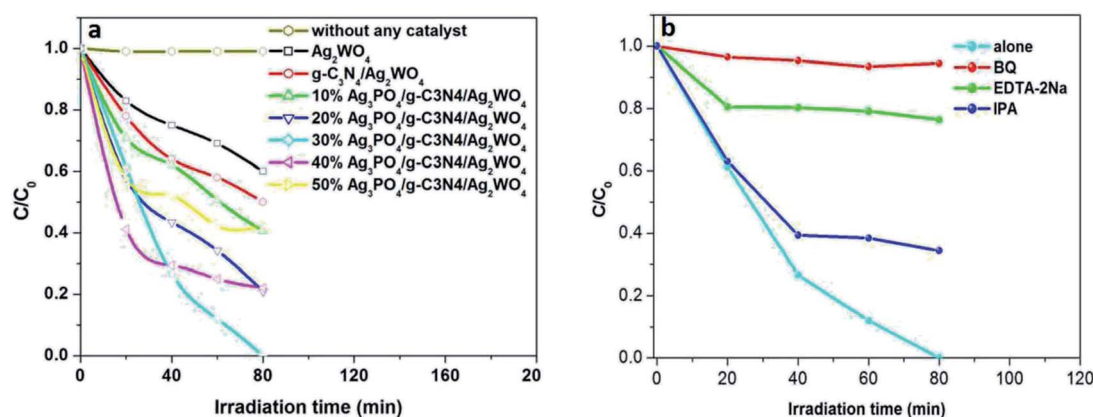


Fig. 7 (a) Photodegradation efficiencies of Rh B as a function of irradiation time for different photocatalysts. (b) Trapping experiment of active species during the photocatalytic degradation of Rh B over  $\text{C}_{60}\text{CNTs}$ /bismuth-based oxide nanocomposites under visible-light irradiation.

electrons on the hydrogen scale (about 4.5 eV),  $E_g$  is the band gap energy of the semiconductor. According to the DRS characterization results (Fig. 6) and eqn (1) and (2), the valence band

(VB) edges of  $\text{g-C}_3\text{N}_4$  QDs,  $\text{Ag}_2\text{WO}_4$ , and  $\text{Ag}_3\text{PO}_4$  were measured to be +1.585, 2.73, and 2.535 eV versus SHE, respectively, while the conduction band (CB) edges for  $\text{g-C}_3\text{N}_4$  QDs,  $\text{Ag}_2\text{WO}_4$ , and  $\text{Ag}_3\text{PO}_4$  were  $-1.165$ ,  $-0.27$ , and  $0.505$  eV versus SHE, respectively.

Fig. 10 shows the proposed mechanism for the charge-carrier transfer process in the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  photocatalyst. When the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite is irradiated, electrons can be excited from CBs of  $\text{g-C}_3\text{N}_4$  QDs and  $\text{Ag}_3\text{PO}_4$ . Because the CB position of  $\text{g-C}_3\text{N}_4$  QDs was more negative than that of  $\text{Ag}_2\text{WO}_4$  and  $\text{Ag}_3\text{PO}_4$ , the photo-generated electrons in the CB of  $\text{g-C}_3\text{N}_4$  QDs can easily flow into the CB of  $\text{Ag}_2\text{WO}_4$  or  $\text{Ag}_3\text{PO}_4$ , leading to the redistribution of electrons and holes so that the oxidation reaction is highly likely to take place and effectively prevent the electron-hole recombination process. Resulting in the improved photocatalytic performance of the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite photocatalyst. The holes in the VB of  $\text{Ag}_3\text{PO}_4$  with strong oxidation power can directly degrade Rh B. In addition, the electrons on the  $\text{g-C}_3\text{N}_4$  can react with  $\text{O}_2$  to produce  $\cdot\text{O}_2^-$ , which can completely oxidize organic molecules to water and carbon dioxide.<sup>31,32</sup>

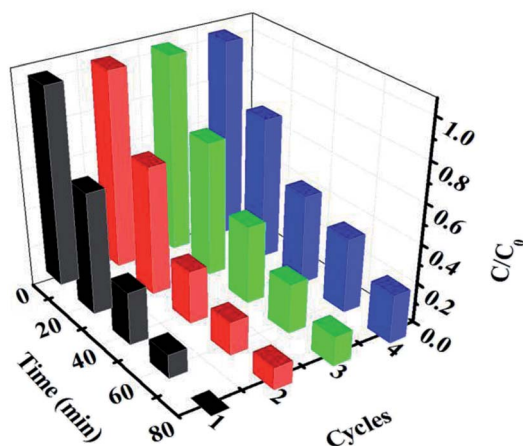


Fig. 8 Cycling runs for the photocatalytic degradation of Rh B over the ternary nanocomposites under visible-light irradiation.



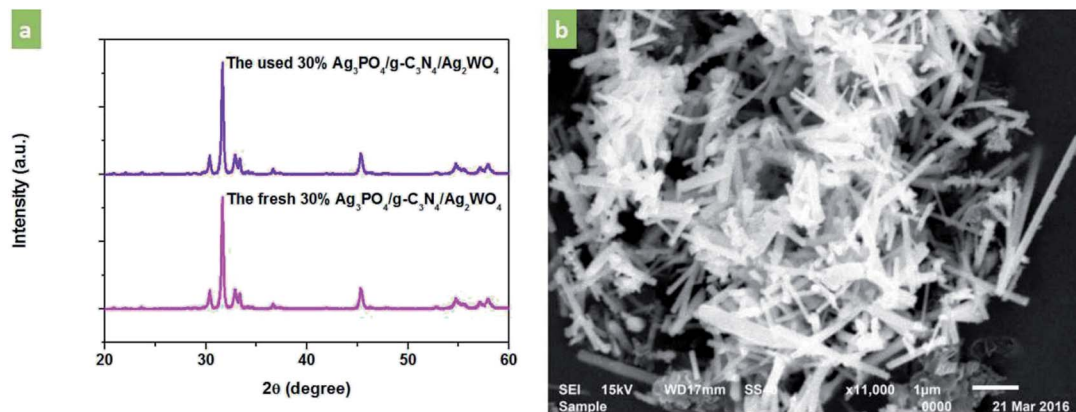


Fig. 9 (a) XRD patterns of the as-prepared 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  sample before and after photocatalysis. (b) SEM image of the 30%  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  sample after photocatalysis.

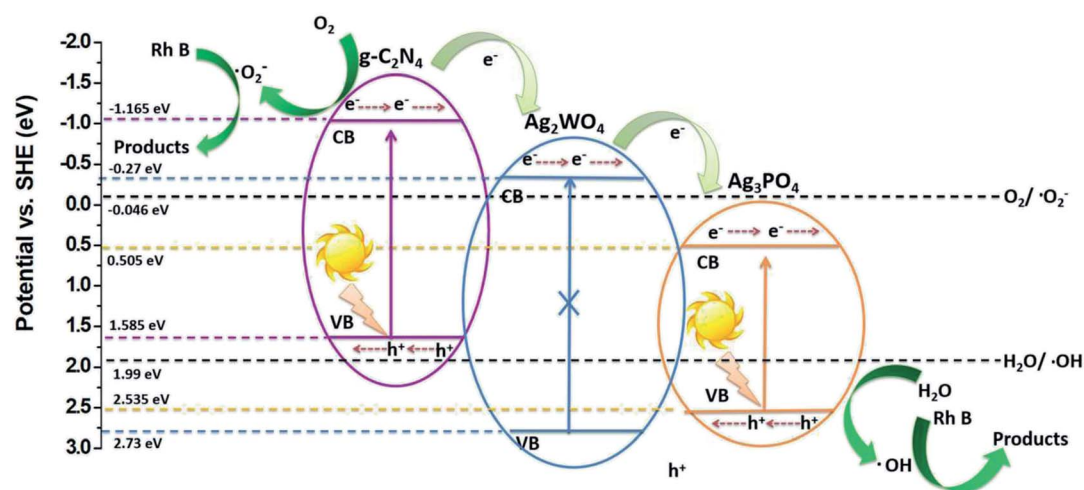


Fig. 10 Schematic diagram of the separation and transfer of photogenerated charges in the  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  composite photocatalyst under visible-light irradiation.

## 4. Conclusions

In summary, novel  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  nanorods were successfully synthesized by using simple deposition-precipitation of  $\text{Ag}_3\text{PO}_4$  nanocrystals and  $\text{g-C}_3\text{N}_4$  QDs on  $\text{Ag}_2\text{WO}_4$  nanorods. The as-prepared  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  nanostructures showed excellent photocatalytic performance on the decolorization of Rh B, which was superior to those of pure  $\text{Ag}_2\text{WO}_4$ , or  $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$  under visible-light irradiation ( $\lambda > 420$  nm). The  $\text{Ag}_3\text{PO}_4$  and  $\text{g-C}_3\text{N}_4$  loading contributed to enhanced visible-light harvesting and reduced recombination of photo-generated electron-hole pairs owing to the synergistic effect of the heterojunction structure of  $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{Ag}_2\text{WO}_4$ , thereby leading to enhanced photocatalytic performance.

## Conflicts of interest

There are no conflicts to declare.

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